Original document

# PRODUCTION OF CHEMICALLY ADSORBED MONOMOLECULAR FILM


Patent number: JP11147074
Publication date: 1999-06-02


Inventor: OGAWA KAZUFUMI; OTAKE TADASHI; NOMURA YUKIO
Applicant: MATSUSHITA ELECTRIC IND CO LTD

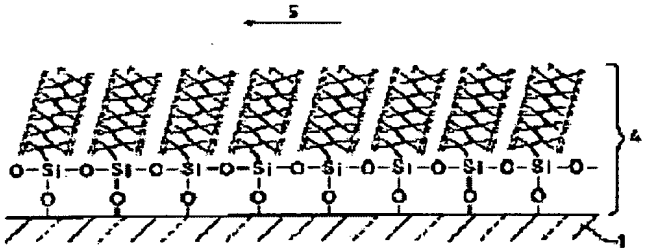

Classification:
- international: B05D7/24; B05D1/18; C08J7/06
- european:
Application number: JP19970317230 19971118
Priority number(s): JP19970317230 19971118


View INPADOC patent family

Report a data error here


Abstract of **JP11147074**

PROBLEM TO BE SOLVED: To form a chemically adsorbed monomolecular film having uniform thickness of a nanometer level within a short time in a highly efficient manner by coating the surface of a substrate with a chemical adsorption soln. containing a non-aq. org. solvent and a silane type surfactant and chemically reacting the surfactant molecules in the adsorption soln. with the surface of the substrate while evaporating and concentrating the org. solvent to bond and fix the molecules to the surface of the substrate at one ends thereof and washing off the unreacted surfactant remaining on the surface of the substrate after the evaporation of the org. solvent. SOLUTION: CF3 (CF2 )7 (CH2 )2 SiCl3 is dissolved in a non-aq. solvent [hexamethylsilicone (b.p.; 100 deg.C)] in a concn. of 1 wt.% to prepare a chemical adsorption soln. and a glass substrate 1 having a transparent electrode formed on the surface thereof is immersed in this soln. and drawn up to evaporate the silicone solvent to concentrate the soln. until the concn. of the chemically adsorbed substance on the surface of the substrate becomes 100%. After the substrate is washed with chloroform, it is drawn up from the washing soln. in the direction shown by a numeral 5 to be drained and exposed to moisture- containing air to form a chemically adsorbed monomolecular film.

---

CLAIMS

---

[Claim(s)]
[Claim 1] The chemisorption liquid prepared using the organic solvent and silane system surfactant of a non-drainage system in the desiccation ambient atmosphere is applied to a base material front face. Carrying out evaporation concentration of said organic solvent, carry out the chemical reaction of the surfactant molecule and substrate front face in said adsorption liquid, and joint immobilization of said surfactant molecule is carried out by the end on a substrate front face. The manufacture approach of the chemisorption monomolecular film characterized by including the process which carries out washing removal of the unreacted surfactant which remained in the substrate front face using the back organic solvent which evaporated said organic solvent.
[Claim 2] The manufacture approach of a chemisorption monomolecular film according to claim 1 of performing the process which carries out washing removal of the unreacted surfactant which used the organic solvent of a non-drainage system and remained in the base material front face after evaporating an organic solvent, and carrying out a predetermined time reaction further.
[Claim 3] The chemisorption liquid prepared using the organic solvent and silane system surfactant of a non-drainage system in the desiccation ambient atmosphere is applied to a substrate front face. Carrying out evaporation concentration of said organic solvent, carry out the chemical reaction of the surfactant molecule and substrate front face in said adsorption liquid, and joint immobilization of said surfactant molecule is carried out by the end on a substrate front face. Washing removal of the unreacted surfactant which remained in the substrate front face using the organic solvent of a non-drainage system after evaporating said organic solvent is carried out. The manufacture approach of the chemisorption monomolecular film characterized by including the process which obtains the chemisorption monomolecular film in which furthermore stood the substrate towards desired, carried out the liquid end of the penetrant remover, the reserve orientation of said fixed molecule was made to carry out in the liquid end direction, and the molecule fixed chemically carried out primary orientation in the fixed direction.
[Claim 4] The manufacture approach of the chemisorption monomolecular film according to claim 3 which carries out washing removal of the unreacted surfactant which used the organic solvent of a non-drainage system and remained in the base material front face after evaporating an organic solvent, and carrying out a predetermined time reaction further.
[Claim 5] The manufacture approach of a chemisorption monomolecular film given in any 1 term of claims 1-4 using the ambient atmosphere of 30% or less of relative humidity as a desiccation ambient atmosphere.
[Claim 6] The manufacture approach of a chemisorption monomolecular film given in any 1 term of claims 1-5 using the surfactant of the silane system which contains a straight chain-like chain or a siloxane joining chain, a chlorosilyl radical, an alkoxysilane radical, or an isocyanate silane radical as a surfactant.
[Claim 7] An end or a part of chain or siloxane joining chain 3 fluoride [ carbon ] radical (-CF3), A methyl group (-CH3), a vinyl group (-CH=CH2), an allyl group (-CH=CH-), An acetylenic group (3-fold association of carbon-carbon), a phenyl group (-C6H5), An aryl group (-C6H4-), a halogen atom, an alkoxy group (-OR;R expresses an alkyl group), A cyano group (-CN), the amino group (-NH2), a hydroxyl group (-OH), a carbonyl group (=CO), The manufacture approach of a chemisorption monomolecular film given in any 1 term of claims 1-6 permuted by at east one organic radical chosen from a carboxy group (-COO-) and a carboxyl group (-COOH).
[Claim 8] The manufacture approach of a chemisorption monomolecular film given in any 1 term of claims 1-7 which mix and use two or more sorts of silicon system surfactants as a surfactant.
[Claim 9] The manufacture approach of a chemisorption monomolecular film given in any 1 term of claims 1-8 which perform the process further exposed through a polarizing plate behind washing or liquid end reserve orientation.
[Claim 10] The manufacture approach of a chemisorption monomolecular film given in any 1 term of claims 1-9 using the solvent which contains an alkyl group, a carbon fluoride radical, a chlorination carbon radical, or a siloxane radical as an organic solvent of a non-drainage system.
[Claim 11] The manufacture approach of the chemisorption monomolecular film according to claim 10 using the solvent of a silicone system as a solvent containing a siloxane radical.

[Claim 12] The manufacture approach of the chemisorption monomolecular film according to claim 10 using the matter whose boiling point is 100-250 degrees C as an organic solvent of a non-drainage system.
[Claim 13] The manufacture approach of a chemisorption monomolecular film offset printing, screen-stencil, or given in any 1 term of claims 1-12 using [ on the process which applies chemisorption liquid, and ] the roll coat method [claim 14] The manufacture approach of the chemisorption monomolecular film according to claim 13 which controlled the viscosity of chemisorption liquid to 1-50000cSt in the process which applies chemisorption liquid when performing offset printing, screen-stencil, or the roll coat method [claim 15] The manufacture approach of the chemisorption monomolecular film according to claim 14 which added silicone to viscosity control of chemisorption liquid

---

[Translation done.]

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of a chemisorption monomolecular film. It is [0002] which is a thing about the manufacture approach of chemisorption monomolecular films which are the thin film materials used with a molecular level, such as a fluorine system antifouling property monomolecular film, orientation film for liquid crystal, polarization film, phase contrast film, and electric conduction film for molecular devices, in more detail.
[Description of the Prior Art] Conventionally, generally as for the manufacture approach of a chemisorption monomolecular film, the approach to be immersed and carry out the time amount chemical reaction of predetermined for a base material between the chemisorption matter in a solvent and a base material front face in a base material front face and the contact interface of chemisorption liquid in said chemisorption liquid has been used for chemisorption liquid.
[0003] For example, the silane system surfactant which contains a straight chain-like hydrocarbon group and Si beforehand Use (it is also hereafter called the chemisorption matter or a chemisorption compound), melt to the solvent of a non-drainage system by about 1% of the weight of concentration, and the chemisorption solution is adjusted. The base material was immersed in this chemisorption liquid, after predetermined carried out the time amount chemisorption reaction in said chemisorption liquid, the base material was picked out from chemisorption liquid, and the approach of carrying out washing removal of the excessive chemisorption liquid adhering to a front face with the organic solvent of a non-drainage system was used, and it came.
[0004]
[Problem(s) to be Solved by the Invention] However, when about 1% of the weight of concentration performed at a room temperature in the creation approach of the conventional chemisorption monomolecular film, about 2 hours was needed and effectiveness was very bad until the reaction was saturated. Then, the approach of raising the concentration of chemisorption liquid or the approach of raising the temperature in chemisorption has been tried as an approach of shortening this reaction time. However, by the approach of heating, about at most 50-60 degrees C is a limitation, and reaction time has been shortened only at most about 10 to 20% in heating of this level. Moreover, when it heated more than it and chemisorption was performed, the solvent evaporated during the adsorption reaction and there were problems, like the orientation of the monomolecular film by which chemisorption was carried out worsens. On the other hand by the approach of raising concentration, the expensive chemisorption matter will be made useless, and effectiveness was bad. Moreover, it was inconvenient also in respect of the stability of the created chemisorption liquid.
[0005] In order that this invention may solve said conventional problem, thickness is very thin on nano meter level, and it aims at offering the approach that a uniform chemisorption monomolecular film can be manufactured in a short time and high efficiency.
[0006]
[Means for Solving the Problem] In order to attain said purpose, as a means to form a monomolecular film in a flat base material or an uneven base material front face in this invention The process which applies to a base material front face the chemisorption liquid prepared using the organic solvent and silane system surfactant of a non-drainage system in the desiccation ambient atmosphere, The process which is made to carry out the chemical reaction of the surfactant molecule and substrate front face in said adsorption liquid, and carries out joint immobilization of said surfactant molecule by the end on a substrate front face, carrying out evaporation concentration of said organic solvent, After evaporation of said organic solvent is completed, the manufacture approach of a chemisorption monomolecular film including the process which carries out washing removal of the unreacted surfactant which remained in the substrate front face using the organic solvent of a non-drainage system is offered. moreover, as a means to form in a flat base material front face the monomolecular film which carried out primary orientation The process which applies to a flat substrate front face at least the chemisorption liquid prepared using the organic solvent and silane system surfactant of a non-drainage system in the desiccation ambient atmosphere, The process which is made to carry out the chemical reaction of the

surfactant molecule and substrate front face in said adsorption liquid, and carries out joint immobilization of said surfactant molecule by the end on a substrate front face, carrying out evaporation concentration of said organic solvent, The manufacture approach of a chemisorption monomolecular film including the process to which carry out washing removal of the unreacted surfactant which remained in the substrate front face using the organic solvent of a non-drainage system, stand a substrate towards desired further, carry out the liquid end of the penetrant remover, and the reserve orientation of said fixed molecule is made to carry out in the liquid end direction is offered.

[0007] After evaporating an organic solvent at this time, if the process which carries out washing removal of the unreacted surfactant which used the organic solvent of a non-drainage system and remained in the base material front face is performed after carrying out a predetermined time reaction further, a chemisorption monomolecular film can be formed still more perfectly.

[0008] Moreover, it is convenient, when the ambient atmosphere of 30% or less of relative humidity is used as a desiccation ambient atmosphere, and manufacturing a perfect chemisorption monomolecular film rather than there is no nebula. Furthermore, it is convenient when shortening reaction time, since activity is high when the surfactant of the silane system which contains a straight chain-like chain or a siloxane joining chain, a chlorosilyl radical, an alkoxysilane radical, or an isocyanate silane radical as a surfactant is used.

[0009] An end or a part of chain or siloxane joining chain further again 3 fluoride [ carbon ] radical (-CF3), A methyl group (-CH3), a vinyl group (-CH=CH2), an allyl group (-CH=CH-), An acetylenic group (3-fold association of carbon-carbon), a phenyl group (-C6H5), an aryl group (-C6H4-), a halogen atom, an alkoxy group (-OR;R expresses an alkyl group and its range of carbon numbers 1-3 is desirable.) If it permutes by at least one organic radical chosen from a cyano group (- CN), the amino group (-NH2), a hydroxyl group (-OH), a carbonyl group (=CO), a carboxy group (-COO-), and a carboxyl group (-COOH) A chemisorption monomolecular film with various surface energy can be created, and it is convenient.

[0010] When two or more sorts of silicon system surface active agents are mixed and used as a surface active agent, a front face can manufacture an uneven monomolecular film with a molecular level and a new function is discovered, it is convenient further again.

[0011] It is convenient when it includes a photosensitive radical in the chemisorption matter, and a molecule, on the other hand, carries out the manufacture approach of the chemisorption monomolecular film by which orientation immobilization was carried out, since orientation of the molecule by which chemisorption was carried out will be carried out along the polarization direction and a polymerization will be carried out, if the process further exposed through a polarizing plate behind adsorption / washing, or liquid end reserve orientation is performed.

[0012] Moreover, if the solvent containing an alkyl group, a carbon fluoride radical, a chlorination carbon radical, or a siloxane radical is used as an organic solvent of a non-drainage system, water content can be lessened sharply, the chemisorption matter can be used more effectively, and it is convenient.

[0013] Furthermore, since there is almost no evaporation residue when the solvent of a silicone system is used as a solvent containing a siloxane radical, a reaction can be gone on more efficiently. It is convenient, when that whose boiling point is 100-250 degrees C is used as an organic solvent of a non-drainage system further again, it is a short time and the solvent evaporation time amount after the time of spreading and spreading is controlled.

[0014] Moreover, in the process which applies chemisorption liquid, if offset printing, screen-stencil, or the roll coat method is used, since chemisorption liquid will not be used beyond the need, a coat can be formed more efficiently.

[0015] Moreover, in the process which applies chemisorption liquid, in case offset printing, screen-stencil, or the roll coat method is performed, when the viscosity of chemisorption liquid is controlled to 1-50000cSt, solvent evaporation time amount after spreading can be shortened, and a liquid lappet can be prevented, and it is convenient. When silicone is used for viscosity control of chemisorption liquid, viscosity can be controlled only by accommodation of molecular weight and it is convenient further again.

[0016]

[The gestalt of invention implementation] The process which applies to a base material front face the chemisorption liquid prepared in the desiccation ambient atmosphere in this invention, using the organic solvent and silane system surfactant of a non-drainage system as the efficient manufacture approach of a chemisorption monomolecular film, The process which is made to carry out the chemical reaction accompanied by elimination reactions, such as demineralization-ized water elementary process and a dealcoholization reaction, for the surfactant molecule and substrate front face in said adsorption liquid, carrying out evaporation concentration of said organic solvent, and carries out joint immobilization of said surfactant molecule by the end on a substrate front face, The process which carries out washing removal of the unreacted surfactant with which said organic solvent remained in the substrate front face using the organic solvent of the non-drainage system after evaporation is included.

[0017] Moreover, the process which applies to a flat substrate front face the chemisorption liquid prepared using the organic solvent and silane system surfactant of a non-drainage system in the desiccation ambient atmosphere, The process which is made to carry out the chemical reaction accompanied by elimination reactions, such as demineralization-ized water elementary process and a dealcoholization reaction, for the surfactant molecule and substrate front face in said adsorption liquid, and carries out joint immobilization of said surfactant molecule by the end on a substrate front face, carrying out evaporation concentration of said organic solvent, The manufacture approach of a chemisorption monomolecular film including the process to which carry out washing removal of the unreacted surfactant which remained in the substrate front face using the organic solvent of a non-drainage system, stand a substrate towards desired further, carry out the liquid end of the penetrant remover, and the reserve orientation of said fixed molecule is made to carry out in the liquid end direction is offered.

[0018]

[Example] This invention is explained still more concretely using an example below.

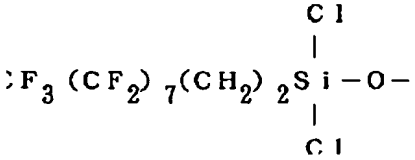
(Example 1) The glass substrate 1 (many hydroxyl groups are included on a front face) with which the transparent electrode was formed in the front face was prepared, and washing cleaning was improved beforehand. Using silane system surfactant (henceforth chemisorption matter or chemisorption compound), and CF3(CF2)7(CH2)2SiCl3 containing the straight chain-like hydrocarbon group and Si which, on the other hand, included in the end one functional group (-CF3 grade) which makes surface energy of a coat small, it melted to the solvent of a non-drainage system by 1% of the weight of concentration, and the chemisorption solution was prepared. At this time, the hexa methyl silicone (if the boiling point was a nonaqueous organic solvent to about 250 degrees C bp.100 degree C and in addition to this, although evaporation time amount became long somewhat, it was usable satisfactory practically in any way.) which dehydrated well was used as a nonaqueous solvent (solvent which does not contain water). Thus, the prepared solution was used as the adsorption solution 2, and grade immersion (you may apply by a coating machine etc.) of said substrate 1 was carried out for 1 minute into this adsorption solution 2 in (30% or less of relative humidity) the desiccation ambient atmosphere ( drawing 1 ). Then, it pulls up from liquid and the silicone solvent was evaporated in this ambient atmosphere, it condensed until the chemisorption matter concentration on the front face of a substrate became 100%, and it was made to react for 10 more minutes after that. That is, the coat which consists only of said chemisorption matter was formed in said substrate front face at 5-micrometer thickness extent, and the reaction on a chemisorption agent and the front face of a substrate was accelerated. Then, after washing using the chloroform 3 which is the solvent of the non-drainage system which does not contain the water dehydrated well in the still more nearly same desiccation ambient atmosphere, it pulled up from the penetrant remover and the liquid end was carried out, and it was exposed into the air which subsequently contains moisture ( drawing 2 ). 5 shows the raising direction from a penetrant remover.

[0019] After the chemisorption monomolecular film 4 to which said chlorosilicane system surfactant comes to react had carried out the chemical bond to the part in which the hydroxyl group on the front face of a substrate was contained through the covalent bond of a siloxane by the above processing, it was formed by about 1nm thickness. In addition, at this time, when the critical table side energy of the chemisorption film was measured using the JISUMAN plot, it was about 10 mN/m. Moreover, the chemisorption monomolecular film which was excellent in a **** and antifouling property about 120 degrees was obtained whenever [ over water / contact angle ].

[0020] It was thought that association of the following formula (** 1) was generated first, it incidentally reacted with the moisture in air in the reaction of a substrate front face and a surfactant when further taken out in general after [ solvent washing ] air, and association of a formula (** 2) was generated. In addition, when the chain of the molecule adsorbed at this time was analyzed by FTIR, it inclined in the liquid end direction (direction opposite to the raising direction 5 from a penetrant remover) to some extent, and orientation of it was carried out to it ( drawing 3 ).

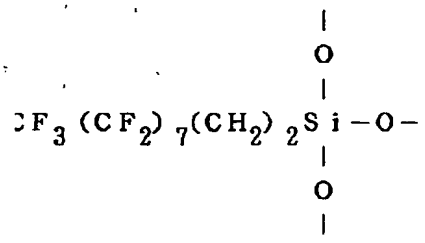
[0021]

[Formula 1]



[0022]

[Formula 2]



[0023] Although opposite peel strength was also checked by the cross cut adhesion test, it did not exfoliate at all further again. In a series of aforementioned chemisorption monomolecular-film formation processes, since it means that it was applied to the substrate front face where said chlorosilicane system surfactant is condensed to 100% after solvent evaporation and the demineralization acid reaction arose in the condition with the SiCl radical of a chlorosilicane system surfactant, and the hydroxyl group on said front face of a substrate, the adsorption time amount usually needed for 1 to 2 hours has been extremely shortened for 11 minutes in a short time.

[0024] (Example 2) The glass substrate (many hydroxyl groups are included on a front face) with which the transparent electrode was formed in the front face was prepared, and washing cleaning was improved beforehand. The silane system surfactant containing the straight chain-like hydrocarbon group and Si which, on the other hand, included one functional group which controls the surface energy of a coat in the end The silane system surfactant incorporating CH(hereafter called chemisorption matter or chemisorption compound) 3 (CH2) 14SiCl3 and a sensitization radical, Using C6H5 CH=CHCOC6H4O(CH2)6SiCl3 (it mixed and used for 1:1 by the mole ratio), it melted to the solvent of a non-drainage system by 1% of the weight of concentration, and the chemisorption solution was adjusted. At this time, the octamethyl silicone (if the boiling point was a nonaqueous organic solvent to about 250 degrees C bp.100 degree C and in addition to this, although evaporation time amount became long somewhat, it was usable satisfactory practically in any way.) which dehydrated well was used as a nonaqueous solvent (solvent which does not contain water). Thus, the prepared solution was used as the adsorption solution and grade immersion (you may apply) of said substrate was carried out for 1 minute into this adsorption solution 2 in (30% or less of relative humidity) the desiccation ambient atmosphere.

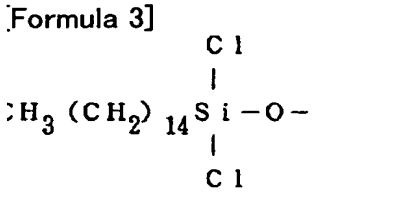
[0025] Then, it pulls up from liquid and the silicone solvent was evaporated in this ambient atmosphere, it condensed until the chemisorption matter concentration on the front face of a substrate became 100%, and it was made to react for 5 more minutes after that. That is, the coat which consists only of said chemisorption matter was formed in said substrate front face, and the reaction on a chemisorption agent and the front face of a substrate was accelerated. Then, after washing using n-hexane which is the solvent of the non-drainage system which does not contain the water dehydrated well in the still more nearly same desiccation ambient atmosphere, where a substrate is stood towards desired, after pulling up from the penetrant remover and carrying out the liquid end, it was exposed into the air containing moisture.

[0026] After chemisorption monomolecular-film 4' to which said mixed chlorosilicane system surfactant comes to react had carried out the chemical bond to the part in which the hydroxyl group on the front face of a substrate was contained through the covalent bond of a siloxane by the above processing, the molecule combined and combined carried out orientation along the raising direction 5 and the opposite direction, i.e., the liquid end direction, and it was formed by about 1.7nm thickness. In addition, the critical table side energy of the chemisorption film was about 28 mN/m at this time.

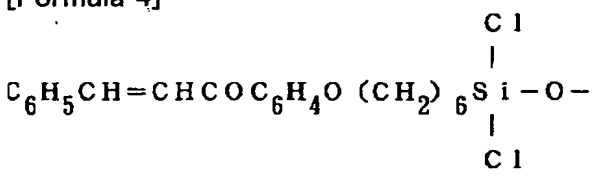
[0027] Then, using two substrates of this condition, it combined so that the chemisorption film might face each other, it set so that the direction of orientation might become antiparallel, the liquid crystal cell of a 20-micron gap was assembled, and when the nematic liquid crystal (ZLI4792; Merck Co. make) was poured in and the orientation condition was checked, the poured-in liquid crystal molecule was carrying out orientation with the abbreviation pre tilt angle of 4 degrees to the substrate toward the liquid end direction of a penetrant remover. It was thought that association of the following formula (** 3 and 4) was generated by about 1:1 ratio, it incidentally reacted with the moisture in air first in the reaction of a substrate front face and a surfactant when further taken out in general after [ solvent washing ] air, and association of a formula (** 5 and 6) was generated. In addition, when the chain of the molecule adsorbed at this time was analyzed by FTIR, it inclined in the liquid end direction to some extent, and orientation of it was carried out to it ( drawing 4 ).

[0028]

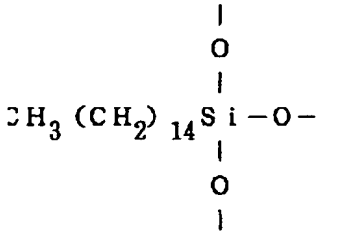
[Formula 3]



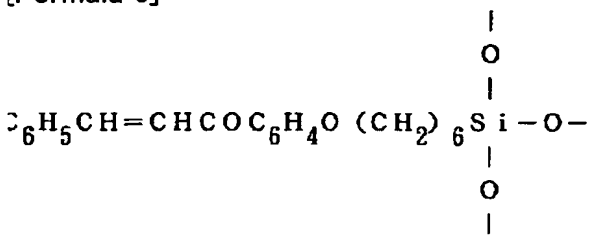
[0029]
[Formula 4]



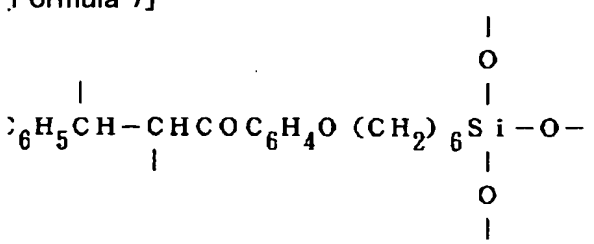
[0030]
[Formula 5]



[0031]
[Formula 6]



[0032] In a series of aforementioned chemisorption monomolecular-film formation processes, since it means that it was applied to the substrate front face where said chlorosilicane system surfactant is condensed to 100% after solvent evaporation and the demineralization acid reaction arose in the condition with the SiCl radical of a chlorosilicane system surfactant, and the hydroxyl group on said front face of a substrate, the adsorption time amount usually needed for 1 to 2 hours has been extremely shortened for 6 minutes in a short time.
[0033] Next, two substrates of this condition were prepared and it could shift 3 times further from each raising direction and the direction which goes direct, namely, the polarizing plate 6 (HNP'B: Polaroid company make) was set to the substrate in piles so that the polarization direction 13 might be suitable in the raising direction and the direction which crosses at 87 degrees, and the 400mJ exposure was carried out using the 365nm (i line) light 7 (after [ polarization film transparency ] 3.6 mW/cm2) of the ultrahigh pressure mercury lamp of 500W ( drawing 5 ). The chemisorption monomolecular film except the polarizing plate 6 after an exposure is shown in drawing 6 . Eight show the direction of reorientation of a film molecule among drawing 6 . Although the molecule which is shown by ** 5 in a chemisorption monomolecular film according to the Fourier transform infrared spectrophotometry did not change with the above processings, since the photosensitive radical (C6H5 CH=CHCOC6H4-) shown ** 6 showed photosensitivity to 365nm (i line) light, it became structure as photopolymerized and shown in ** 7. Nine express a transparent electrode among drawing 5 - 6. Moreover, the structure of a film molecule is shown in drawing 7 . 4" shows the chemisorption monomolecular film with which the polymerization of the photosensitive radical by which reorientation was carried out was carried out among drawing 7 .
[0034]
[Formula 7]



[0035] Furthermore, using two substrates of this condition, it combined so that chemisorption film 4" of drawing 7 might face each other, it set so that the direction of orientation might become antiparallel, the liquid crystal cell of a 20-micron gap was assembled, and when the nematic liquid crystal (ZLI4792; Merck Co. make) was poured in and the orientation condition was checked, the poured-in liquid crystal molecule was carrying out

orientation with the abbreviation pre tilt angle of 4 degrees to the substrate along the polarization direction.
[0036] Incidentally, if the direction of orientation of the straight chain-like chain in said chemisorption monomolecular-film 4' was analyzed using FTIR, although critical table side energy and a tilt angle did not change, the direction 8 of orientation changed almost as in parallel as the polarization direction 13, and, moreover, orientation dispersion is also improved from the time of the liquid end reserve orientation by raising.
[0037] In addition, in order to arrange the direction of orientation of the admolecule of the exposure section with an one direction at this time, the liquid end direction is not completely intersected at 90 degrees, but it can be necessary to shift some more than abundance preferably. If 90 degrees is made to intersect completely, each molecule may turn to a 2-way. In addition, when the polarization direction 13 was doubled so that it might become the penetrant remover liquid end direction and parallel, the monomolecular film which was further excellent in orientation restraining force was obtained.
[0038] moreover, to change the direction of orientation alternatively on a substrate front face After performing the raising liquid end beforehand, if ultraviolet rays with a wavelength of 365nm are irradiated with the energy of 200-500mJ in piles, a pattern-like mask to a polarizing plate Respectively along with the part from which the direction of orientation changes and only the irradiated part differs in the shape of a pattern within the orientation film within the same side in the direction of orientation, i.e., the raising liquid end direction 5 and the polarization direction 13, liquid crystal was able to prepare two or more parts which carry out orientation.
[0039] In addition, when the ambient atmosphere of 35% or more of relative humidity was used as a desiccation ambient atmosphere, even if washed, the coat remained in the substrate front face white, and it was not able to remove easily. Moreover, the reaction rate has used it, although the surfactant which contains an alkoxysilane radical or an isocyanate silane radical although the surfactant of the silane system which contains a straight chain-like chain or a siloxane joining chain, and a chlorosilyl radical as a surfactant was used also became a little late.
[0040] Two or more sorts of silicon system surfactants with which critical table side energy differs as a surfactant further again, An end or a part of chain or siloxane joining chain For example, 3 fluoride [ carbon ] radical (-CF3), A methyl group (-CH3), a vinyl group (-CH=CH2), an allyl group (-CH=CH-), An acetylenic group (3-fold association of carbon-carbon), a phenyl group (-C6H5), an aryl group (-C6H4-), a halogen atom, an alkoxy group (-OR;R expresses an alkyl group and its range of carbon numbers 1-3 is desirable.) A cyano group (- CN), the amino group (-NH2), a hydroxyl group (-OH), When the surfactant permuted by at least one organic radical chosen from a carbonyl group (=CO), a carboxy group (-COO-), and a carboxyl group (-COOH) was used, critical table side energy has been controlled in the range of 10 - 55 dyn/cm very easily.
[0041] Moreover, the unreacted surfactant was efficiently removable when the solvent containing an alkyl group, a carbon fluoride radical, a chlorination carbon radical, or a siloxane radical was used as an organic solvent of a non-drainage system.
[0042] When the presentation of CH3 (CH2)14SiCl3 and C6H5 CH=CHCOC6H4O(CH2)6SiCl3 was changed by 1:0-0:1 (preferably 50:1 - 1:50) at this time, critical table side energy changed to 35 mN/m from 24 mN/m, and the pre tilt angle has been controlled in 86 to 3 degrees to arbitration, respectively. Furthermore, when it added, the surfactant 3 which contains a fluorine as a chemisorption compound instead of, for example, CF3(CF2)7 (CH2)2SiCl, and went, critical table side energy was able to be small done to 14 mN/m. [ CH3 (CH2)14SiCl3 ] In 20-% of the weight addition, although the pre tilt angle of liquid crystal was about 90 degrees, when the electrical potential difference was impressed and driven, a very uniform orientation change was shown.
[0043] In addition, the approach of applying adsorption liquid 2 to the substrate front face 1 by the desired pattern using offset printing, screen-stencil, or the roll coat method has been used to form the film in a substrate front face alternatively.
[0044] As mentioned above, although chain length mixed and used the silane system surfactant of -(CH2) 14-, and the silane system surfactant which has a photosensitive radical by -(CH2) 6- in the example 1 Even if it mixed and used the surface active agent with which the die length of chain length differs (-(CH2) n-;n is the integer of the range of 1 to 25), the direction of orientation could be controlled by the polarization direction, and was controlled whenever [ pre tilt angle ] by critical table side energy of a monomolecular film similarly. Moreover, although the siloxane joining chain (-(SiO) n-;n is the integer of the range of 1 to 15) was incorporated instead of the hydrocarbon chain, the same orientation control was possible.
[0045] In addition, although the 365nm light which is i line of an ultrahigh pressure mercury lamp as a light used for exposure was used in the above-mentioned example 2, it is also possible to use light (436nm, 405nm, 254nm, and 248nm obtained with a KrF excimer laser) according to the absorption-of-light degree of the film matter. Since especially light (248nm and 254nm) tends to be absorbed by most matter, its energy orientation effectiveness is high.
[0046] (Example 3) In the example 1, the adsorption solution which melted and produced the compound containing two or more chlorosilyl radicals in (30% or less of relative humidity) the dry ambient atmosphere before the process which performs chemisorption of the surfactant molecule containing a chain or a siloxane

joining chain was made, and it applied to the substrate front face and dried. then, the compound which an adsorption solvent evaporates and contains two or more chlorosilyl radicals is condensed -- having -- just -- being alike -- the coat of the compound containing two or more chlorosilyl radicals was formed. At this time, the chlorosilyl radical of the compound containing two or more hydroxyl groups contained on the substrate front face and chlorosilyl radicals carries out a demineralization acid reaction quickly. Then, when the organic solvent of the non-drainage system which hardly contains moisture further washed and having been taken out in air, the chlorosilyl radical which remained in the substrate front face reacted with the moisture in air, and the chemisorption monomolecular film which consists of SiOH association, i.e., the inorganic siloxane containing many hydroxyl groups, was formed in the front face.

[0047] For example, melt 1% of the weight in the toluene which considered as the silyl compound containing two or more Krol radicals, and dehydrated using Cl3SiOSiCl3, and adsorption liquid is produced. Since a substrate is immersed about 1 minute and it pulls up further in a desiccation ambient atmosphere, and grade-applies for 5 minutes, it dries in this ambient atmosphere and toluene is evaporated, if the chloroform dehydrated still better [ after making it react for 5 minutes ] washes Since - OH radical was contained for some in the base material front face, the coat 11 of the shape of a monomolecular film as a demineralization acid reaction produced in an interface and shown in drawing 8 was formed in the substrate front face through -SiO-association. It took out in air further after that, and when it was made to react with the moisture in air, the siloxane coat 12 of the shape of a monomolecular film containing many hydroxyl groups (- OH) was formed in the front face as shown in drawing 9 on the substrate front face through -SiO-association.

[0048] In a series of aforementioned chemisorption monomolecular-film formation processes, since it means that it was applied to the substrate front face where the silyl compound which contains two or more said Krol radicals after solvent evaporation is condense to 100% and the demineralization acid reaction arose in the condition with the SiCl radical of a chlorosilicane system surfactant, and the hydroxyl group on said front face of a substrate, the chemisorption time amount usually need for 1 to 2 hours has be extremely shorten for 11 minutes in a short time.

[0049] In addition, since it is completely combined with the substrate through the chemical bond of -SiO-, the siloxane monomolecular film 12 made at this time does not separate. Moreover, the obtained monomolecular film has many SiOH association in a front face. Especially as for - OH radical, the about about 2 to 3 times [ of the beginning ] number was generated. The processing section in this condition had the very high hydrophilic property.

[0050] Then, when the chemisorption process was performed in this condition using the same surfactant as an example 1, after the chemisorption monomolecular film which contains the chain to which CF3(CF2)7(CH2)2SiCl3 surfactant comes to react like 4 of drawing 1 had carried out the chemical bond by the covalent bond of a siloxane through said siloxane monomolecular film 12, it was formed by about 1.8nm thickness. At this time, about about 2 to 3 times, and since many [ compared with an example 1 ], the adsorption site on the front face of a base material before adsorption of a surfactant (in this case, OH radical) was able to enlarge the admolecule consistency more compared with the case of an example 1. Moreover, the processing section had very high oil repellency.

[0051] In addition, it considers as the silyl compound containing two or more Krol radicals, and is Cl-(SiCl2O) n-SiCl3 (n is an integer.) in addition to said Cl3SiOSiCl3. However, 0, 1-3 were easy to treat. It has used.

[0052] (Example 4) In the example 2, when ClSi(CH3)2OSi(CH3)2OSi(CH3)2OSi(CH3)2Cl was mixed and used between 1:0-0:1 instead of CH3 (CH2)14SiCl3 as chemisorption matter, critical table side energy has been controlled in the range of 37 mN/m to 23 mN/m according to the mixing ratio.

[0053] (Example 5) As chemisorption matter, instead of CH3 (CH2)14SiCl3, CH3CH2 C*HCH3CH2OCO(CH2) 10SiCl3 (however, C* irregular carbon) was mixed and used between 1:0-1:20, and the same orientation film was produced in the example 2. In this case, critical table side energy was controllable in the range of 31 mN/m to 41 mN/m according to the mixing ratio.

[0054]

[Effect of the Invention] According to this invention, thickness is very thin on nano meter level, and the effectiveness which is a short time very much and can form the chemisorption monomolecular film excellent in thickness homogeneity efficient has it as explained above.

---

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平11－147074

(43)公開日　平成11年(1999)６月２日

| (51)Int.Cl.[6] | | 識別記号 | FI | | |
|---|---|---|---|---|---|
| Ｂ０５Ｄ | 7/24 | ３０２ | Ｂ０５Ｄ | 7/24 | ３０２Ｙ |
| | 1/18 | | | 1/18 | |
| Ｃ０８Ｊ | 7/06 | | Ｃ０８Ｊ | 7/06 | |

審査請求　未請求　請求項の数15　ＯＬ　（全９頁）

(21)出願番号　特願平9－317230

(22)出願日　平成９年(1997)11月18日

(71)出願人　000005821
松下電器産業株式会社
大阪府門真市大字門真1006番地

(72)発明者　小川　一文
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(72)発明者　大竹　忠
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(72)発明者　野村　幸生
大阪府門真市大字門真1006番地　松下電器産業株式会社内

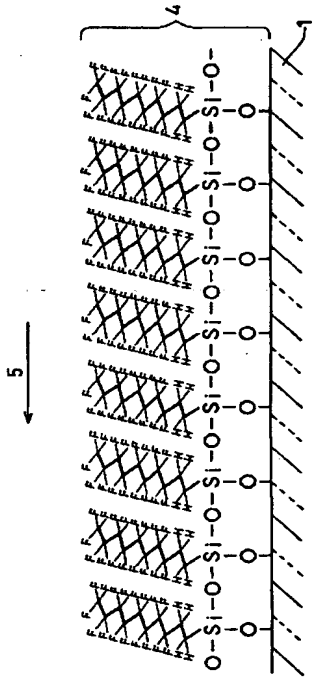
(74)代理人　弁理士　池内　寛幸　（外１名）

(54)【発明の名称】　化学吸着単分子膜の製造方法

(57)【要約】

【課題】非水系の有機溶媒とシラン系界面活性剤を含む化学吸着液を基材表面に塗布し、有機溶媒を蒸発濃縮させつつ吸着液中の界面活性剤分子と基板表面とを化学反応させて分子を基板表面に一端で結合固定し、有機溶媒を蒸発させた後基板表面に残った未反応の界面活性剤を洗浄除去することにより、ナノメータレベルの厚さの均一な化学吸着単分子膜を短時間で高能率に形成する。

【解決手段】$CF_3(CF_2)_7(CH_2)_2SiCl_3$を１重量%の濃度で非水系の溶媒(ヘキサメチルシリコーン（ｂｐ．１００℃)に溶かして化学吸着溶液とし、この中に表面に透明電極の形成されたガラス基板１を浸漬し、液から引き上げて、シリコーン溶媒を蒸発させ、基板表面の化学吸着物質濃度が１００%になるまで濃縮し、クロロホルムを用いて洗浄した後洗浄液より引き上げて液切りし、次いで水分を含む空気中に暴露し、化学吸着単分子膜４を形成する。



【特許請求の範囲】
【請求項１】　乾燥雰囲気中で非水系の有機溶媒とシラン系界面活性剤を用いて調製した化学吸着液を基材表面に塗布し、前記有機溶媒を蒸発濃縮させつつ前記吸着液中の界面活性剤分子と基板表面とを化学反応させ前記界面活性剤分子を基板表面に一端で結合固定し、前記有機溶媒を蒸発させた後有機溶媒を用い基板表面に残った未反応の界面活性剤を洗浄除去する工程とを含むことを特徴とする化学吸着単分子膜の製造方法。
【請求項２】　有機溶媒を蒸発させた後、さらに所定時間反応させた後に非水系の有機溶媒を用い基材表面に残った未反応の界面活性剤を洗浄除去する工程を行う請求項１に記載の化学吸着単分子膜の製造方法。
【請求項３】　乾燥雰囲気中で非水系の有機溶媒とシラン系界面活性剤を用いて調製した化学吸着液を基板表面に塗布し、前記有機溶媒を蒸発濃縮させつつ前記吸着液中の界面活性剤分子と基板表面とを化学反応させ前記界面活性剤分子を基板表面に一端で結合固定し、前記有機溶媒を蒸発させた後非水系の有機溶媒を用い基板表面に残った未反応の界面活性剤を洗浄除去し、さらに所望の方向に基板を立てて洗浄液を液切りし、液切り方向に前記固定された分子を予備配向させ、化学的に固定された分子が一定方向に一次配向した化学吸着単分子膜を得る工程を含むことを特徴とする化学吸着単分子膜の製造方法。
【請求項４】　有機溶媒を蒸発させた後、さらに所定時間反応させた後に非水系の有機溶媒を用い基材表面に残った未反応の界面活性剤を洗浄除去する請求項３に記載の化学吸着単分子膜の製造方法。
【請求項５】　乾燥雰囲気として相対湿度３０％以下の雰囲気を用いた請求項１～４のいずれか１項に記載の化学吸着単分子膜の製造方法。
【請求項６】　界面活性剤として直鎖状炭素鎖またはシロキサン結合鎖とクロロシリル基またはアルコキシシラン基またはイソシアネートシラン基を含むシラン系の界面活性剤を用いた請求項１～５のいずれか１項に記載の化学吸着単分子膜の製造方法。
【請求項７】　炭素鎖またはシロキサン結合鎖の末端または一部が、３フッ化炭素基（－$CF_3$）、メチル基（－$CH_3$）、ビニル基（－CH＝$CH_2$）、アリル基（－CH＝CH－）、アセチレン基（炭素－炭素の３重結合）、フェニル基（－$C_6H_5$）、アリール基（－$C_6H_4$－）、ハロゲン原子、アルコキシ基（－ＯＲ；Ｒはアルキル基を表す）、シアノ基（－ＣＮ）、アミノ基（－$NH_2$）、水酸基（－ＯＨ）、カルボニル基（＝ＣＯ）、カルボキシ基（－ＣＯＯ－）及びカルボキシル基（－ＣＯＯＨ）から選ばれる少なくとも一つの有機基で置換されている請求項１～６のいずれか１項に記載の化学吸着単分子膜の製造方法。
【請求項８】　界面活性剤として複数種のシリコン系界面活性剤を混合して用いる請求項１～７のいずれか１項に記載の化学吸着単分子膜の製造方法。
【請求項９】　洗浄後、または液切り予備配向後、さらに偏光板を介して露光する工程を行う請求項１～８のいずれか１項に記載の化学吸着単分子膜の製造方法。
【請求項１０】　非水系の有機溶媒として、アルキル基、ふっ化炭素基または塩化炭素基またはシロキサン基を含む溶媒を用いた請求項１～９のいずれか１項に記載の化学吸着単分子膜の製造方法。
【請求項１１】　シロキサン基を含む溶媒としてシリコーン系の溶媒を用いた請求項１０に記載の化学吸着単分子膜の製造方法。
【請求項１２】　非水系の有機溶媒として、沸点が１００～２５０℃の物質を用いた請求項１０に記載の化学吸着単分子膜の製造方法。
【請求項１３】　化学吸着液を塗布する工程において、オフセット印刷、スクリーン印刷、またはロールコート法を用いた請求項１～１２のいずれか１項に記載の化学吸着単分子膜の製造方法
【請求項１４】　化学吸着液を塗布する工程において、オフセット印刷、スクリーン印刷、またはロールコート法を行う際、化学吸着液の粘度を１～５００００ｃＳｔに制御した請求項１３に記載の化学吸着単分子膜の製造方法
【請求項１５】　化学吸着液の粘度制御にシリコーンを添加した請求項１４に記載の化学吸着単分子膜の製造方法
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、化学吸着単分子膜の製造方法に関するものである。さらに詳しくは、フッ素系防汚性単分子膜、液晶用配向膜、偏光膜、位相差膜、分子素子用導電膜など、分子レベルで用いる薄膜材料である化学吸着単分子膜の製造方法に関するものである
【０００２】
【従来の技術】従来、化学吸着単分子膜の製造方法は、化学吸着液に基材を浸漬し、前記化学吸着液中で基材表面と化学吸着液の接触界面において、すなわち溶媒中の化学吸着物質と基材表面間において所定の時間化学反応させる方法が一般的に用いられてきた。
【０００３】例えば、あらかじめ直鎖状炭化水素基及びＳｉを含むシラン系界面活性剤（以下、化学吸着物質あるいは化学吸着化合物ともいう）を用い、１重量％程度の濃度で非水系の溶媒に溶かして化学吸着溶液を調整しておき、この化学吸着液に基材を浸漬し、前記化学吸着液中で所定の時間化学吸着反応させた後化学吸着液から基材を取り出し、表面に付着した余分の化学吸着液を非水系の有機溶媒で洗浄除去する方法が用いられたきた。
【０００４】

【発明が解決しようとする課題】しかしながら、従来の化学吸着単分子膜の作成方法では、１重量％程度の濃度で室温で行う場合、反応が飽和するまでおよそ２時間程度を必要とし極めて効率が悪かった。そこで、この反応時間を短縮する方法として、化学吸着液の濃度を上げる方法、あるいは化学吸着中の温度を上げる方法が試みられてきた。ところが、加熱する方法では、せいぜい５０～６０℃程度が限界であり、この程度の加熱では高々１０～２０％程度しか反応時間を短縮できなかった。また、それ以上加熱して化学吸着を行うと、吸着反応中溶媒が蒸発してしまったり、化学吸着された単分子膜の配向が悪くなるなどの問題があった。一方、濃度を上げる方法では、高価な化学吸着物質を無駄にすることになり効率が悪かった。また、作成された化学吸着液の安定性の面でも不都合であった。

【０００５】本発明は、前記従来の問題を解決するため、厚みはナノメータレベルできわめて薄く、均一な化学吸着単分子膜を短時間、高能率に製造できる方法を提供することを目的とする。

【０００６】

【課題を解決するための手段】前記目的を達成するため、本発明では、平坦な基材や凸凹な基材表面に単分子膜を形成する手段として、乾燥雰囲気中で非水系の有機溶媒とシラン系界面活性剤を用いて調製した化学吸着液を基材表面に塗布する工程と、前記有機溶媒を蒸発濃縮させつつ前記吸着液中の界面活性剤分子と基板表面とを化学反応させ前記界面活性剤分子を基板表面に一端で結合固定する工程と、前記有機溶媒の蒸発が終了した後非水系の有機溶媒を用い基板表面に残った未反応の界面活性剤を洗浄除去する工程とを含む化学吸着単分子膜の製造方法を提供する。また、平坦な基材表面に一次配向した単分子膜を形成する手段として、少なくとも、乾燥雰囲気中で非水系の有機溶媒とシラン系界面活性剤を用いて調製した化学吸着液を平坦な基板表面に塗布する工程と、前記有機溶媒を蒸発濃縮させつつ前記吸着液中の界面活性剤分子と基板表面とを化学反応させ前記界面活性剤分子を基板表面に一端で結合固定する工程と、非水系の有機溶媒を用い基板表面に残った未反応の界面活性剤を洗浄除去し、さらに所望の方向に基板を立てて洗浄液を液切りし、液切り方向に前記固定された分子を予備配向させる工程を含む化学吸着単分子膜の製造方法を提供する。

【０００７】このとき、有機溶媒を蒸発させた後、さらに所定時間反応させた後に非水系の有機溶媒を用い基材表面に残った未反応の界面活性剤を洗浄除去する工程を行うとさらに完璧に化学吸着単分子膜を形成できる。

【０００８】また、乾燥雰囲気として相対湿度３０％以下の雰囲気を用いると、白濁がないより完璧な化学吸着単分子膜を製造する上で都合がよい。さらに、界面活性剤として直鎖状炭素鎖またはシロキサン結合鎖とクロロシリル基またはアルコキシシラン基またはイソシアネートシラン基を含むシラン系の界面活性剤を用いると活性度が高いので反応時間を短縮する上で都合がよい。

【０００９】さらにまた、炭素鎖またはシロキサン結合鎖の末端または一部が、３フッ化炭素基（$-CF_3$）、メチル基（$-CH_3$）、ビニル基（$-CH=CH_2$）、アリル基（$-CH=CH-$）、アセチレン基（炭素－炭素の３重結合）、フェニル基（$-C_6H_5$）、アリール基（$-C_6H_4-$）、ハロゲン原子、アルコキシ基（－ＯＲ；Ｒはアルキル基を表し、炭素数１～３の範囲が好ましい。）、シアノ基（－ＣＮ）、アミノ基（$-NH_2$）、水酸基（－ＯＨ）、カルボニル基（＝ＣＯ）、カルボキシ基（－ＣＯＯ－）及びカルボキシル基（－ＣＯＯＨ）から選ばれる少なくとも一つの有機基で置換されていると、いろいろな表面エネルギーをもつ化学吸着単分子膜を作成できて好都合である。

【００１０】さらにまた、界面活性剤として複数種のシリコン系界面活性剤を混合して用いると、表面が分子レベルで凸凹な単分子膜を製造でき、新たな機能を発現する上で都合がよい。

【００１１】一方、化学吸着物質に感光性基を組み込み、吸着・洗浄後、または液切り予備配向後、さらに偏光板を介して露光する工程を行うと、化学吸着された分子は偏光方向に沿って配向され且つ重合されるので、分子が配向固定された化学吸着単分子膜を製造方法する上で都合がよい。

【００１２】また、非水系の有機溶媒として、アルキル基、ふっ化炭素基または塩化炭素基またはシロキサン基を含む溶媒を用いると含水率を大幅に少なくできて、化学吸着物質をより有効に使用できて都合がよい。

【００１３】さらに、シロキサン基を含む溶媒としてシリコーン系の溶媒を用いると蒸発残査がほとんど無いのでより効率的に反応を進行できる。さらにまた、非水系の有機溶媒として、沸点が１００～２５０℃のものを用いると、塗布時および塗布後の溶媒蒸発時間を短時間で且つ制御する上で都合がよい。

【００１４】また、化学吸着液を塗布する工程において、オフセット印刷、スクリーン印刷、またはロールコート法を用いると、必要以上に化学吸着液を使用しないのでより効率よく被膜を形成できる。

【００１５】また、化学吸着液を塗布する工程において、オフセット印刷、スクリーン印刷、またはロールコート法を行う際、化学吸着液の粘度を１～５００００ｃＳｔに制御しておくと、塗布後の溶媒蒸発時間を短くでき、且つ液垂れを防ぐことができて都合がよい。さらにまた、化学吸着液の粘度制御にシリコーンを用いると、分子量の調節のみで粘度を制御できて都合がよい。

【００１６】

【発明実施の形態】本発明では、化学吸着単分子膜の効率よい製造方法として、乾燥雰囲気中で非水系の有機溶

媒とシラン系界面活性剤を用いて調製した化学吸着液を基材表面に塗布する工程と、前記有機溶媒を蒸発濃縮させつつ前記吸着液中の界面活性剤分子と基板表面とを脱塩化水素反応、脱アルコール反応等の脱離反応を伴う化学反応をさせ、前記界面活性剤分子を基板表面に一端で結合固定する工程と、前記有機溶媒が蒸発後非水系の有機溶媒を用い基板表面に残った未反応の界面活性剤を洗浄除去する工程とを含む。

【００１７】また、乾燥雰囲気中で非水系の有機溶媒とシラン系界面活性剤を用いて調製した化学吸着液を平坦な基板表面に塗布する工程と、前記有機溶媒を蒸発濃縮させつつ前記吸着液中の界面活性剤分子と基板表面とを脱塩化水素反応、脱アルコール反応等の脱離反応を伴う化学反応をさせ前記界面活性剤分子を基板表面に一端で結合固定する工程と、非水系の有機溶媒を用い基板表面に残った未反応の界面活性剤を洗浄除去し、さらに所望の方向に基板を立てて洗浄液を液切りし、液切り方向に前記固定された分子を予備配向させる工程を含む化学吸着単分子膜の製造方法を提供する。

【００１８】

【実施例】以下実施例を用いて本発明をさらに具体的に説明する。

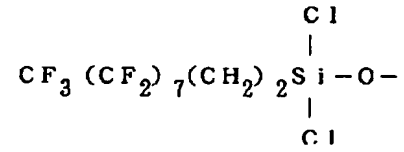
（実施例１）表面に透明電極の形成されたガラス基板１（表面に水酸基を多数含む）を準備し、あらかじめよく洗浄脱脂した。一方、末端に被膜の表面エネルギーを小さくする官能基（－$CF_3$等）を一つ組み込んだ直鎖状炭化水素基及びＳｉを含むシラン系界面活性剤（以下、化学吸着物質あるいは化学吸着化合物ともいう）、$CF_3(CF_2)_7(CH_2)_2SiCl_3$を用い、１重量％の濃度で非水系の溶媒に溶かして化学吸着溶液を調製しておいた。このとき、非水系溶媒（水を含まない溶媒）としては、良く脱水したヘキサメチルシリコーン（ｂｐ．１００℃、これ以外に、沸点が２５０℃程度までの非水系有機溶媒なら、多少蒸発時間が長くはなるが実用上、何ら問題なく使用可能であった。）を用いた。このようにして調製された溶液を吸着溶液２とし、乾燥雰囲気中（相対湿度３０％以下）で、この吸着溶液２の中に前記基板１を１分間程度浸漬（コーター等で塗布しても良い）した（図１）。その後、液から引き上げて、同雰囲気中でシリコーン溶媒を蒸発させ、基板表面の化学吸着物質濃度が１００％になるまで濃縮し、その後さらに１０分間反応させた。すなわち、前記化学吸着物質のみからなる被膜を前記基板表面に５μｍ膜厚程度に形成し化学吸着剤と基板表面の反応を加速させた。その後、さらに同様の乾燥雰囲気中で良く脱水した水を含まない非水系の溶媒であるクロロホルム３を用いて洗浄した後洗浄液より引き上げて液切りし、次いで水分を含む空気中に暴露した（図２）。５は洗浄液からの引き上げ方向を示す。

【００１９】以上の処理により、前記クロロシラン系界面活性剤が反応してなる化学吸着単分子膜４が基板表面の水酸基が含まれていた部分にシロキサンの共有結合を介して化学結合した状態で約１ｎｍの膜厚で形成された。なお、このとき化学吸着膜の臨界表面エネルギーは、ジスマンプロットを用いて測定すると約１０ｍＮ／ｍであった。また、水に対する接触角度は１２０度程度有り、防汚性に優れた化学吸着単分子膜が得られた。

【００２０】ちなみに、基板表面と界面活性剤との反応においては、はじめに下記式（化１）の結合が生成され、さらに、溶媒洗浄後一般空気中に取り出すと、空気中の水分と反応して式（化２）の結合が生成されたものと考えられた。なお、このとき吸着された分子の炭素鎖はＦＴＩＲで分析すると液切り方向（洗浄液からの引き上げ方向５と反対の方向）にある程度傾斜して配向していた（図３）。

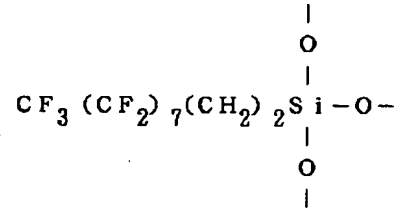
【００２１】

【化１】



【００２２】

【化２】



【００２３】さらにまた、対剥離強度も碁盤目試験で確認したが全く剥離しなかった。前記の一連の化学吸着単分子膜形成工程において、溶媒蒸発後には前記クロロシラン系界面活性剤が１００％に濃縮された状態で基板表面に塗布されたことになり、その状態でクロロシラン系界面活性剤のＳｉＣｌ基と前記基板表面の水酸基とで脱塩酸反応が生じるので、通常１～２時間必要とする吸着時間が、１１分間と極めて短時間に短縮できた。

【００２４】（実施例２）表面に透明電極の形成されたガラス基板（表面に水酸基を多数含む）を準備し、あらかじめよく洗浄脱脂した。一方、末端に被膜の表面エネルギーを制御する官能基を一つ組み込んだ直鎖状炭化水素基及びＳｉを含むシラン系界面活性剤（以下、化学吸着物質あるいは化学吸着化合物ともいう）、$CH_3(CH_2)_{14}SiCl_3$と感光基を組み込んだシラン系界面活性剤、$C_6H_5CH=CHCOC_6H_4O(CH_2)_6SiCl_3$（モル比で１：１に混合して用いた）を用い、１重量％の濃度で非水系の溶媒に溶かして化学吸着溶液を調整しておいた。このとき、非水系溶媒（水を含まない溶

媒）としては、良く脱水したオクタメチルシリコーン（ｂｐ．１００℃、これ以外に、沸点が２５０℃程度までの非水系有機溶媒なら、多少蒸発時間が長くはなるが実用上、何ら問題なく使用可能であった。）を用いた。このようにして調製された溶液を吸着溶液とし、乾燥雰囲気中（相対湿度３０％以下）で、この吸着溶液２の中に前記基板を１分間程度浸漬（塗布しても良い）した。

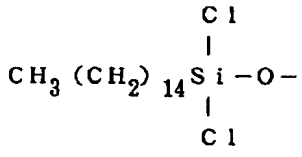
【００２５】その後、液から引き上げて、同雰囲気中でシリコーン溶媒を蒸発させ、基板表面の化学吸着物質濃度が１００％になるまで濃縮し、その後さらに５分間反応させた。すなわち、前記化学吸着物質のみからなる被膜を前記基板表面に形成し化学吸着剤と基板表面の反応を加速させた。その後、さらに同様の乾燥雰囲気中で良く脱水した水を含まない非水系の溶媒であるｎ－ヘキサンを用いて洗浄した後、基板を所望の方向に立てた状態で洗浄液より引き上げて液切りした後、水分を含む空気中に暴露した。

【００２６】以上の処理により、前記混合クロロシラン系界面活性剤が反応してなる化学吸着単分子膜４’が基板表面の水酸基が含まれていた部分にシロキサンの共有結合を介して化学結合した状態で結合され、結合された分子が引き上げ方向５と反対方向、すなわち液切り方向に沿って配向して約１．７ｎｍの膜厚で形成された。なお、このとき化学吸着膜の臨界表面エネルギーは約２８ｍＮ／ｍであった。

【００２７】そこで、この状態の基板２枚を用い、化学吸着膜が向かい合うように組み合わせて、配向方向がアンチパラレルになるようにセットし２０ミクロンギャップの液晶セルを組み立て、ネマチック液晶（ＺＬＩ４７９２；メルク社製）を注入して配向状態を確認すると、注入した液晶分子が洗浄液の液切り方向に向かって、基板に対して約プレチルト角４°で配向していた。ちなみに、基板表面と界面活性剤との反応においては、はじめに下記式（化３および４）の結合がほぼ１：１の比で生成され、さらに、溶媒洗浄後一般空気中に取り出すと、空気中の水分と反応して式（化５及び６）の結合が生成されたものと考えられた。なお、このとき吸着された分子の炭素鎖はＦＴＩＲで分析すると液切り方向にある程度傾斜して配向していた（図４）。

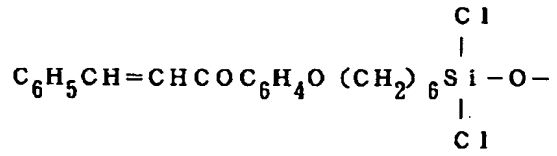
【００２８】

【化３】



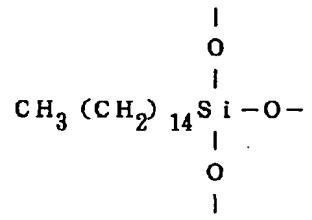
【００２９】

【化４】



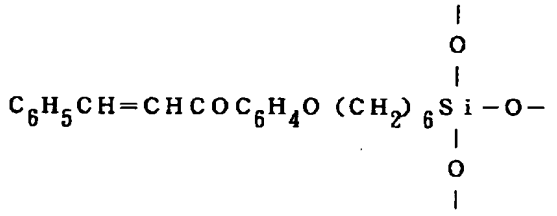
【００３０】

【化５】



【００３１】

【化６】

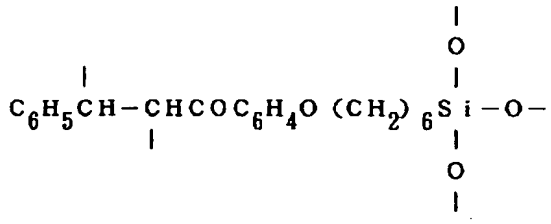


【００３２】前記の一連の化学吸着単分子膜形成工程において、溶媒蒸発後には前記クロロシラン系界面活性剤が１００％に濃縮された状態で基板表面に塗布されたことになり、その状態でクロロシラン系界面活性剤のＳｉＣｌ基と前記基板表面の水酸基とで脱塩酸反応が生じるので、通常１～２時間必要とする吸着時間が、６分間と極めて短時間に短縮できた。

【００３３】次に、この状態の基板を２個用意し、さらにそれぞれの引き上げ方向と直行する方向から３度ずらせて、即ち引き上げ方向と８７度で交差する方向に偏光方向１３が向くように偏光板６（ＨＮＰ’Ｂ：ポラロイド社製）を基板に重ねてセットし、５００Ｗの超高圧水銀灯の３６５ｎｍ（ｉ線）の光７（偏光膜透過後３．６ｍＷ／ｃｍ²）を用いて４００ｍＪ照射した（図５）。照射後の偏光板６を除いた化学吸着単分子膜を図６に示す。図６中、８は膜分子の再配向方向を示す。以上の処理により、ＦＴＩＲ分析によると化学吸着単分子膜内の化５で示される分子は変化しないが、化６示される感光性基（$C_6H_5CH=CHCOC_6H_4-$）は、３６５ｎｍ（ｉ線）の光に感光性を示すので、光重合して化７に示したような構造となった。図５～６中、９は透明電極を表わす。また膜分子の構造を図７に示す。図７中、４”は再配向された感光性基が重合された化学吸着単分子膜を示す。

【００３４】

【化７】



【００３５】さらに、この状態の基板２枚を用い、図７の化学吸着膜４”が向かい合うように組み合わせて、配向方向がアンチパラレルになるようにセットし２０ミクロンギャップの液晶セルを組み立て、ネマチック液晶（ＺＬＩ４７９２；メルク社製）を注入して配向状態を確認すると、注入した液晶分子が偏光方向に沿って、基板に対して約プレチルト角４°で配向していた。

【００３６】ちなみに、前記化学吸着単分子膜４’中の直鎖状炭素鎖の配向方向をＦＴＩＲを用いて分析すると臨界表面エネルギーとチルト角は変わらなかったが配向方向８は偏光方向１３とほぼ平行方向に変化し、しかも配向ばらつきも、引き上げによる液切り予備配向時より改善されていた。

【００３７】なお、このとき照射部の吸着分子の配向方向を一方向に揃えるためには、液切り方向と完全に９０°で交差するのではなく、多少、好ましくは数度以上ずらせる必要がある。もし万一、完全に９０°に交差させれば、個々の分子が２方向に向いてしまう場合がある。なお、洗浄液液切り方向と平行になるように偏光方向１３を合わせると、さらに配向規制力の優れた単分子膜が得られた。

【００３８】また、基板表面で選択的に配向方向を変えたい場合には、あらかじめ引き上げ液切りを行った後、偏光板にパターン状のマスクを重ねて２００～５００ｍＪのエネルギーで３６５ｎｍの波長の紫外線を照射すると、照射された部分のみ配向方向が変化し同一面内の配向膜内でパターン状に配向方向の異なる部分、すなわち、引き上げ液切り方向５と偏光方向１３にそれぞれ沿って液晶が配向する部分を複数箇所設けることができた。

【００３９】なお、乾燥雰囲気として相対湿度３５％以上の雰囲気を用いた場合には、洗浄しても基板表面に白く被膜が残り簡単には除去できなかった。また、界面活性剤として直鎖状炭素鎖またはシロキサン結合鎖とクロロシリル基を含むシラン系の界面活性剤を用いたが、アルコキシシラン基またはイソシアネートシラン基を含む界面活性剤も反応速度はやや遅くなるが、利用できた。

【００４０】さらにまた、界面活性剤として臨界表面エネルギーの異なる複数種のシリコン系界面活性剤、例えば炭素鎖またはシロキサン結合鎖の末端または一部が、３フッ化炭素基（－$CF_3$）、メチル基（－$CH_3$）、ビニル基（－CH＝$CH_2$）、アリル基（－CH＝CH－）、アセチレン基（炭素－炭素の３重結合）、フェニル基（－$C_6H_5$）、アリール基（－$C_6H_4$－）、ハロゲン原子、アルコキシ基（－ＯＲ；Ｒはアルキル基を表し、炭素数１～３の範囲が好ましい。）、シアノ基（－ＣＮ）、アミノ基（－$NH_2$）、水酸基（－ＯＨ）、カルボニル基（＝ＣＯ）、カルボキシ基（－ＣＯＯ－）及びカルボキシル基（－ＣＯＯＨ）から選ばれる少なくとも一つの有機基で置換されている界面活性剤を用いると臨界表面エネルギーを１０～５５ｄｙｎ／ｃｍの範囲で極めて簡単に制御できた。

【００４１】また、非水系の有機溶媒として、アルキル基、ふっ化炭素基または塩化炭素基またはシロキサン基を含む溶媒を用いると未反応の界面活性剤を効率よく除去できた。

【００４２】このとき、$CH_3(CH_2)_{14}SiCl_3$と$C_6H_5CH=CHCOC_6H_4O(CH_2)_6SiCl_3$の組成を１：０～０：１（好ましくは５０：１～１：５０）で変えると、臨界表面エネルギーは２４ｍＮ／ｍから３５ｍＮ／ｍに変化し、それぞれプレチルト角は８６°から３°の範囲で任意に制御できた。さらに、$CH_3(CH_2)_{14}SiCl_3$の代わりに化学吸着化合物としてフッ素を含む界面活性剤、例えば、$CF_3(CF_2)_7(CH_2)_2SiCl_3$を添加して行くと臨界表面エネルギーは１４ｍＮ／ｍまで小さくできた。２０重量％添加の場合は、液晶のプレチルト角はほぼ９０度であったが、電圧を印加して駆動してみると、きわめて均一な配向変化を示した。

【００４３】なお、膜を基板表面に選択的に形成したい場合には、オフセット印刷、スクリーン印刷、またはロールコート法を用いて所望のパターンで基板表面１に吸着液２を塗布する方法が利用できた。

【００４４】以上のように、実施例１では、炭素鎖長が－$(CH_2)_{14}$－のシラン系界面活性剤と－$(CH_2)_6$－で感光性基を有するシラン系界面活性剤とを混合して用いたが、炭素鎖長の長さが異なる（例えば、－$(CH_2)_n$－；ｎは１から２５の範囲の整数）界面活性剤を混合して用いても、配向方向は偏光方向で制御でき、プレチルト角度は単分子膜の臨界表面エネルギーで同様に制御できた。また炭化水素鎖の代わりにシロキサン結合鎖（－$(SiO)_n$－；ｎは１から１５の範囲の整数）を組み込んでも同様の配向制御が可能であった。

【００４５】なお、上記実施例２では、露光に用いる光として超高圧水銀灯のｉ線である３６５ｎｍの光を用いたが、膜物質の光の吸収度合いに応じて４３６ｎｍ、４０５ｎｍ、２５４ｎｍやＫｒＦエキシマレーザーで得られる２４８ｎｍの光を用いることも可能である。特に、２４８ｎｍや２５４ｎｍの光は大部分の物質に吸収され易いためエネルギー配向効率が高い。

【００４６】（実施例３）実施例１に於て、炭素鎖やシロキサン結合鎖を含む界面活性剤分子の化学吸着を行う工程の前に、ドライ雰囲気中（相対湿度３０％以下）で

クロロシリル基を複数個含む化合物を溶かして作製した吸着溶液を作り、基板表面に塗布し乾燥した。すると、吸着溶媒が蒸発しクロロシリル基を複数個含む化合物は濃縮され、ついにはクロロシリル基を複数個含む化合物の皮膜が形成された。このとき、基板表面に含まれた水酸基とクロロシリル基を複数個含む化合物のクロロシリル基が急速に脱塩酸反応する。その後、さらに水分をほとんど含まない非水系の有機溶媒で洗浄し、空気中に取り出すと、基板表面に残ったクロロシリル基が空気中の水分と反応して、表面にＳｉＯＨ結合、すなわち水酸基を多数含む無機シロキサンから成る化学吸着単分子膜が形成された。

【００４７】たとえば、クロル基を複数個含むシリル化合物として$Cl_3SiOSiCl_3$を用い脱水したトルエンに１重量％溶かして吸着液を作製し、乾燥雰囲気中で基板を１分程度浸漬し、さらに引き上げて同雰囲気中で５分間程度かけて乾燥しトルエンを蒸発させてからさらに５分反応させた後よく脱水したクロロホルムで洗浄すると、基材表面には－ＯＨ基が多少とも含まれているので、界面で脱塩酸反応が生じ図８に示したような単分子膜状の被膜１１が、－ＳｉＯ－結合を介して基板表面に形成された。その後さらに空気中に取り出し、空気中の水分と反応させると図９に示したような表面に水酸基（－ＯＨ）を多数含む単分子膜状のシロキサン被膜１２が－ＳｉＯ－結合を介して基板表面に形成された。

【００４８】前記の一連の化学吸着単分子膜形成工程において、溶媒蒸発後には前記クロル基を複数個含むシリル化合物が１００％に濃縮された状態で基板表面に塗布されたことになり、その状態でクロロシラン系界面活性剤のＳｉＣｌ基と前記基板表面の水酸基とで脱塩酸反応が生じるので、通常１～２時間必要とする化学吸着時間が、１１分間と極めて短時間に短縮できた。

【００４９】なお、このときできたシロキサン単分子膜１２は基板とは－ＳｉＯ－の化学結合を介して完全に結合されているので剥がれることが無い。また、得られた単分子膜は表面にＳｉＯＨ結合を数多く持つ。特に－ＯＨ基は、当初の約２～３倍程度の数が生成された。この状態での処理部は、極めて親水性が高かった。

【００５０】そこで、この状態で、実施例１と同様の界面活性剤を用い化学吸着工程を行うと、図１の４と同様、$CF_3(CF_2)_7(CH_2)_2SiCl_3$界面活性剤が反応してなる炭素鎖を含む化学吸着単分子膜が前記シロキサン単分子膜１２を介してシロキサンの共有結合で化学結合した状態で約１．８ｎｍの膜厚で形成された。このとき、界面活性剤の吸着前の基材表面の吸着サイト（この場合はＯＨ基）は、実施例１に比べて約２～３倍程度と多いため、実施例１の場合に比べより吸着分子密度を大きくできた。また、処理部は極めて撥油性が高かった。

【００５１】なお、クロル基を複数個含むシリル化合物として、前記$Cl_3SiOSiCl_3$以外に$Cl-(SiCl_2O)_n-SiCl_3$（ｎは整数。ただし０，１～３が扱いよかった。）が利用できた。

【００５２】（実施例４）実施例２に於て、化学吸着物質として$CH_3(CH_2)_{14}SiCl_3$の代わりに、$ClSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2Cl$を１：０～０：１の間で混合して用いた場合、臨界表面エネルギーは混合比に応じて３７ｍＮ／ｍから２３ｍＮ／ｍの範囲で制御できた。

【００５３】（実施例５）実施例２に於て、化学吸着物質として$CH_3(CH_2)_{14}SiCl_3$の代わりに、$CH_3CH_2C^*HCH_3CH_2OCO(CH_2)_{10}SiCl_3$（ただし、Ｃ*は不整炭素）を１：０～１：２０の間で混合して用い同様の配向膜を作製した。この場合には、臨界表面エネルギーは混合比に応じて３１ｍＮ／ｍから４１ｍＮ／ｍの範囲で制御できた。

【００５４】

【発明の効果】以上説明した通り、本発明によれば、厚みはナノメータレベルできわめて薄く、膜厚均一性に優れた化学吸着単分子膜を極めて短時間で、高効率に形成できる効果がある。

【図面の簡単な説明】

【図１】　本発明の実施例１における単分子膜作製に用いる化学吸着工程を説明するための断面概念図。

【図２】　同、単分子膜作製の洗浄工程を説明するための断面概念図。

【図３】　同、溶媒洗浄後のフッ素系単分子膜内の分子配向状態を説明するために断面を分子レベルまで拡大した概念図。

【図４】　本発明の実施例２における感光性基を組み込んだ単分子膜内の分子配向状態を説明するために断面を分子レベルまで拡大した概念図。

【図５】　同、光露光により吸着された分子を再配向させるために用いた露光工程の概念図。

【図６】　同、光配向後の単分子膜内の分子配向状態を説明するための概念図。

【図７】　同、光配向後の化学吸着単分子膜の分子配向状態を説明するために断面を分子レベルまで拡大した概念図。

【図８】　本発明の実施例３におけるクロロシラン単分子膜の形成された状態（空気中の水分との反応前）を説明するために分子レベルまで拡大した断面概念図。

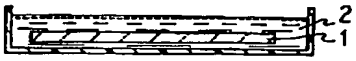
【図９】　本発明の実施例３におけるシロキサン単分子膜の形成された状態を説明するために分子レベルまで拡大した断面概念図。

【符号の説明】

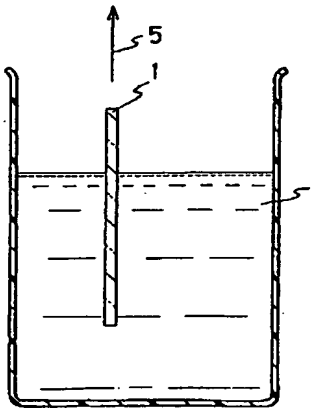
１　基板
２　化学吸着液
３　洗浄用非水系溶媒
４　フッ素系化学吸着単分子膜

４’　１次配向された感光性基を有する化学吸着単分子膜
４”　再配向された感光性基が重合された化学吸着単分子膜
５　洗浄液からの引き上げ方向
６　偏光板
７　照射光
８　再配向方向
９　透明電極
１１　単分子膜状のクロロシラン被膜
１２　単分子膜状のシロキサン被膜
１３　偏光方向

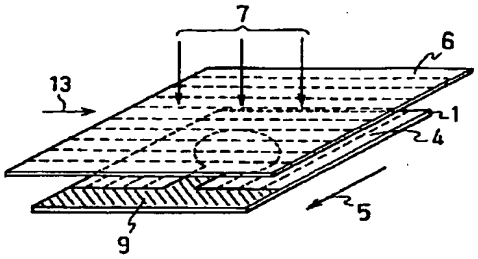
【図１】



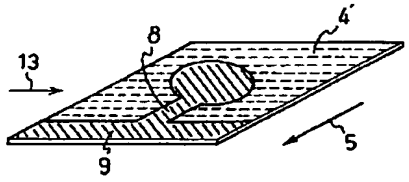

【図２】



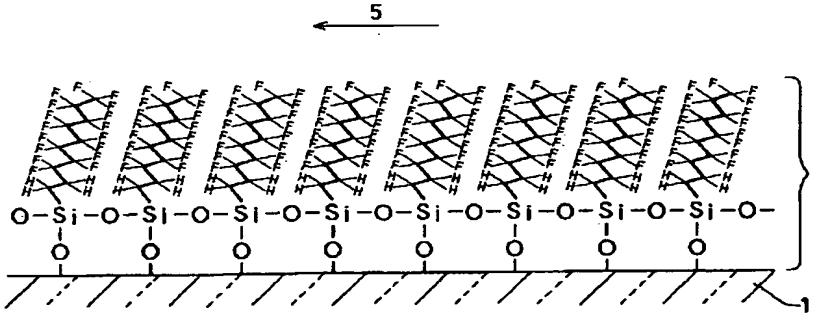

【図５】



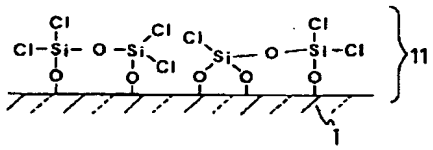

【図６】



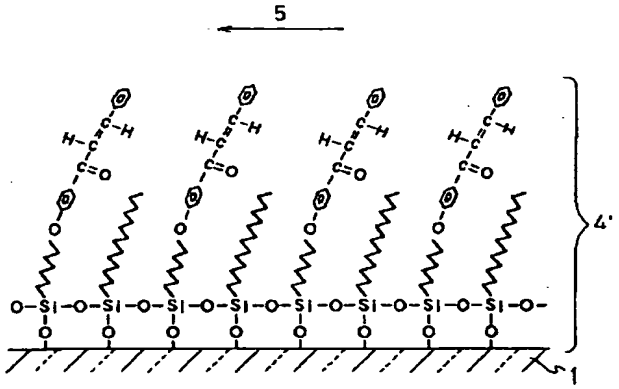

【図３】



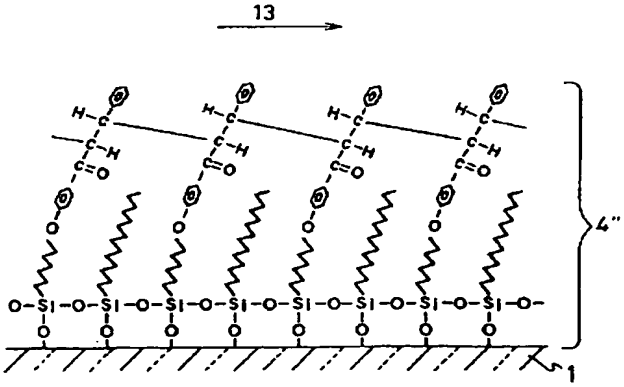

【図８】



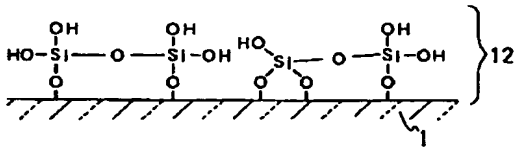

【図４】




【図７】



【図9】



# BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

**IMAGES ARE BEST AVAILABLE COPY.**
**As rescanning documents *will not* correct images problems checked, please do not report the problems to the IFW Image Problem Mailbox**